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COLLABORATIVE STUDY OF METHOD FOR STACK GAS ANALYSIS AND DETERMINATION OF MOISTURE FRACTION WITH USE OF METHOD 5

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Southwest Research Institute

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16. ABSTRACT

Statistical analyses are performed on data from EPA Method 3 (Stack Gas Analysis for Carbon Dioxide, Excess Air and Dry Molecular Weight) and from the stack gas moisture fraction determination obtained in the collaborative testing of EPA Method 5 (Particulates). Using data from Method 5 tests at a Portland cement plant, a coal-fired power plant and a municipal incinerator, estimation is made of the precision that can be expected with the use of these methods. For Method 3, the precision of CO_2 and O_2 determination using an Orsat analyzer is investigated, as well as the effect of this on the dry molecular weight and excess air calculations. In addition, the effect of variability in CO_2 and O_2 determinations on correcting particulate determinations to a common base is studied. The precision of the determination of the moisture fraction of the stack gas by the formula in Method 5 is studied. Recommendations are made for the improvement of the precision of the Orsat method.

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SUMMARY AND CONCLUSIONS

This report presents the analyses of data which were obtained in the performance of EPA Method 3 (Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight) and in the determination of stack moisture content with the use of EPA Method 5 for particulate matter determination. The data were obtained during collaborative testing of Method 5.

The collaborative tests were conducted at a Portland cement plant, a coal-fired power plant, and a municipal incinerator, using four sampling teams at each site. For this study, each sampling run at a test site is considered a repetition at the same true level for both the stack gas analysis and the moisture determination. This assumption is made since there were no independent methods for the determination of true values, and since at a given site there were no significant changes in the determined values. At the cement plant, power plant, and incinerator, there were 15, 16, and 12 runs, respectively. Not all collaborators completed all runs, and thus there were missing values for the statistical analyses. A total of 160 Method 3 determinations and 150 moisture determinations were submitted to statistical treatment.

Precision estimates are obtained for the various parameters, with the exception of excess air, from an analysis of variance based on a nested experimental design. These estimates are expressed in terms of within-laboratory, laboratory bias, and between-laboratory components, and are presented below in terms of standard deviations. Since the actual gas composition undoubtedly varied slightly from run to run, with within-laboratory components contain source variations as well as sampling error and are probably larger than would be expected in the use of these analytical procedures in the field. The laboratory bias component is essentially free of this added variation due to the manner in which it is calculated. The results obtained for each component are summarized below.

Method 3 - All collaborators used Orsat apparatus to perform their stack gas analyses. The average of three consecutive analyses was used, but the requirement that they differ by no more than 0.2% by volume was not enforced. There was no detectable CO at any of the test sites:

(1) *CO_2*. The within-laboratory standard deviation is estimated as 1.44% CO_2 by volume, with 149 degrees of freedom. The laboratory bias standard deviation is estimated as 1.06% CO_2, with 9 degrees of freedom. This gives a between-laboratory standard deviation of 1.78% CO_2. Particulate concentrations from compliance tests at municipal incinerators are corrected to 12% CO_2. The demonstrated variation in a CO_2 determination would cause the reported particulate concentrations of two laboratories who obtained the same uncorrected particulate concentrations to differ from each other by 36% at low CO_2 levels, and 16% at high CO_2 levels.

(2) *O_2*. The within-laboratory standard deviation for O_2 is estimated as 1.70% O_2 by volume, with 149 degrees of freedom. The laboratory bias standard deviation is estimated as 1.29% O_2, with 9 degrees of freedom. This results in an estimated between-laboratory standard deviation of 2.14% O_2.

(3) *Dry Molecular Weight.* The within-laboratory standard deviation for dry molecular weight determination is 0.20 lb/lb-mole with 149 degrees of freedom. The estimated laboratory bias standard deviation is 0.14 lb/lb-mole with 9 degrees of freedom. From these, the between-laboratory standard deviation is estimated as 0.24 lb/lb-mole. Thus, this determination is precise, even though there is considerable variation in the CO_2 and O_2 values used in the calculation.

(4) *Excess Air.* The excess air determination is shown to be a function of the O_2 level, increasing exponentially as the % O_2 increases. The least squares estimation of the model is

$$\% EA = (10.47)e^{(0.21)(\% O_2)}$$

with a coefficient of determination, r^2, of 0.993. The equation was obtained using one quarter of the excess air values from the three sites. From this model and the precision demonstrated for % O_2, normal deviation in % O_2 determination can be expected to produce a variation of from 30% to 60% in the excess air value.

Moisture Fraction –The within-laboratory standard deviation is estimated as 0.032 with 140 degrees of freedom. The laboratory bias standard deviation estimate is 0.032 with 8 degrees of freedom. This gives a between-laboratory standard deviation of 0.045.

The following conclusions and recommendations are made based upon the results presented above:

(1) In a great deal of compliance testing, Method 3 is used only for the determination of the dry molecular weight of the stack gas, i.e., the CO_2 and excess air values are not used in subsequent calculations. When this is the case, the requirement that 3 consecutive analyses differ by no more than 0.2% by volume may be relaxed. The precision shown for the dry molecular weight in this study without the restriction would be sufficient for field tests usage.

(2) When correction factors based upon the Orsat analysis are to be used, e.g. correction to 12% CO_2 or correction for excess air, it is imperative that the stack gas composition be determined precisely. Small variations in the CO_2 and O_2 levels can produce relatively large variations in these factors, and thus three consecutive analyses differing by no more than 0.2% by volume is a reasonable requirement.

(3) To allow more precise determination of stack gas composition, two relatively simple modifications of the standard Orsat gas analyzer could be made.

   (a) The gas buret could be modified to allow direct reading to 0.1 mℓ, with interpolation to the nearest 0.05 mℓ.

   (b) A more accurate method of adjusting the pressure in the gas buret to atmospheric pressure could be installed. The present hand-held leveling bulb could be replaced with a leveling bulb mounted in a screw-adjustable leveling clamp. Incorporation of a small sidearm manometer at the top of the buret would allow precise adjustment of the pressure via the screw adjustment on the leveling clamp. Installation of a stopcock in the sidearm manometer would be necessary to block off the manometer during filling of the gas buret and during transfer of the gas to and from the absorbing burets.

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I. INTRODUCTION

This report describes the work performed on Contracts 68-02-0623 and 68-02-0626 and the results obtained on Southwest Research Institute Project 01-3462-008, Contract 68-02-0626, which includes collaborative testing of the method for stack gas analysis and the method for determination of stack gas moisture fraction with use of Method 5 for particulate emissions as given in "Standards of Performance for New Stationary Sources"[1].

This report describes the statistical analysis of the data from collaborative tests conducted at a Portland cement plant,[2] a coal-fired power plant[3], and a municipal incinerator[4].

The collaborative tests of the method for stack gas analysis and the method for determination of the stack gas moisture fraction were not conducted as separate tests of Methods 3 and 4 [1] but as these methods are used in conjunction with Method 5 for particulate emissions.

The results of the data analyses and the conclusions and recommendations based on these analyses are given in this report.

II. TEST DESCRIPTION

A. Collaborative Test Sites

The site of the Portland cement plant test was the Lone Star Industries Portland Cement Plant in Houston, Texas. This plant utilizes the wet feed process and operates three kilns. The flue gas from each kiln passes through a separate electrostatic precipitator. The flue gases are then combined and feed into a 300-foot-high stack.[2] Samples were taken at the sample ports located on the stack 150 feet above grade.

Typical stack gas composition was about 7.5% CO_2 and 13.5% O_2. No CO was detected. Moisture fraction (B_{wo}) was about 0.25.

The site of the coal-fired power plant was the Allen King Power Plant, The Northern States Power Company, near St. Paul, Minnesota. The exhaust gas from the combustion chamber passes through the heat exchanger and splits into two identical streams upstream of twin electrostatic precipitators. The twin emission gas streams are fed into an 800-foot-high stack through two horizontal ducts.[3]

Samples were taken from sample ports located in the south horizontal duct upstream of the entrance to the stack flue. Typical stack gas composition was about 11.8% CO_2 and 6.4% O_2. No CO was detected. Moisture fraction (B_{wo}) was about 0.10.

The site for the municipal incinerator test was the Holmes Road Incinerator, City of Houston, Houston, Texas. The facility consists of two independent parallel furnace trains. Refuse feeds continuously onto traveling grate stokers in the furnaces. Gases leaving the furnaces are cooled in water spray chambers, and then enter the flue gas scrubbers to remove particulates. The gases are then drawn through induced draft fans and exhaust into the 148-foot-high stacks. Samples were taken from the sample ports located on the stacks 102 feet above grade. During the test, samples were taken from both units at the incinerator. Typical stack gas composition was about 5.2% CO_2 and 14.1% O_2. No CO was detected. Moisture fraction (B_{wo}) was about 0.40.

Stack gas samples were taken at all three sites during the performance of Method 5 determinations. Equal quantities of gas were taken at each traverse point to provide an integrated sample. Stack gas was transferred from the stack to a gas sample bag by means of a one-way squeeze bulb. Stack gas samples were analyzed by the Orsat procedure after each day's runs.

Moisture determination was made by the impinger method in conjunction with the Method 5 determinations.

B. Collaborators and Test Personnel

The collaborators for the Lone Star Industries Portland Cement Plant test were Mr. Charles Rodriguez and Mr. Nollie Swynnerton of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Mike Taylor and Mr. Ron Hawkins of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Quirino Wong, Mr. Randy Creighton, and Mr. Vito Pacheco, Department of Public Health, City of Houston, Houston, Texas; and Mr. Royce Alford, Mr. Ken Drummond, and Mr. Lynn Cochran of Southwestern Laboratories, Austin, Texas.

The collaborators for the Allen King Power Plant test were Mr. Mike Taylor and Mr. Hubert Thompson of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Gilmore Sem, Mr. Vern Goetsch, and Mr. Jerry Brazelli of Thermo-Systems, Inc, St. Paul, Minn.; and Mr. Roger Johnson and Mr. Harry Patel of Environmental Research Corporation, St. Paul, Minn.

The collaborators for the Holmes Road Incinerator test were Mr. Mike Taylor and Mr. Rick Hohmann of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Quirino Wong, Mr. Randy Creighton, and

Mr. Steve Byrd, City of Houston, Department of Public Health; Mr. John Key, Mr. James Draper, Mr. Tom McMickle, Mr. Tom Palmer, Mr. Michael Lee, and Mr. Charles Goerner, Air Pollution Control Services, Texas State Department of Health.*

The Portland cement plant test was conducted under the supervision of Dr. Henry Hamil, and the power plant and municipal incinerator tests were conducted under the supervision of Mr. Nollie Swynnerton, both of Southwest Research Institute.

Collaborators for all three tests were selected by Dr. Hamil.

*Throughout the remainder of this report, the collaborative laboratories are referred to by randomly assigned code numbers. For the cement plant test, code numbers 101, 102, 103, and 104 are used. For the power plant test, code numbers 201, 202, 203, and 204 are used. For the cement plant test, code numbers 301, 302, 303, and 304 are used. These numbers do not correspond to the above ordered listing of laboratories. The ordering is the order that was used in the particulate collaborative studies. The first digit has been changed to correspond to the site numbers used in this report.

III. STATISTICAL DESIGN

A. Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The estimates of the pertinent values are developed in the subsequent sections.

We say that an estimator, $\hat{\theta}$, is *unbiased* for a parameter θ if the expected value of $\hat{\theta}$ is θ, or in notational form, $E(\hat{\theta}) = \theta$. From a population of method determinations made at the same true level, μ, let $x_1, x_2, \ldots, x_n$ be a sample of n replicates. Then we define:

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean*, an unbiased estimate of the *true mean of the population of determinations*, δ. The sample mean gives an estimate of the center of the distribution of the determinations. If the method is accurate, δ is equal to μ, the true level.

(2) $SS = \sum_{i=1}^{n} (x_i - \bar{x})^2$ as the *sum of squares* for the sample, which is used to estimate the dispersion of the population of determinations around δ.

(3) df as the *degrees of freedom*, an indication of the amount of confidence in the estimate. A larger number of df implies more confidence in the estimate.

(4) $\hat{\sigma}^2 = SS/df$, as a *variance estimate*, or *mean square*, unbiased for σ^2, *the true variance of the determinations*. The variance is a measure of the dispersion in the determinations around the true mean, δ.

(5) $\hat{\sigma} = \sqrt{\hat{\sigma}^2}$, as the estimated standard deviation of the determinations. This term is a biased estimate of $\sigma = \sqrt{\sigma^2}$ and is an alternative measure of dispersion.

The variability in a method determination is expressed in terms of *within-laboratory*, *laboratory bias* and *between-laboratory* components. The following definitions of these terms are given with respect to a *true value*, μ.

- *Within-laboratory* –The within-laboratory component measures the dispersion in replicate single method determinations of the same true value, μ, made by one laboratory. The within-laboratory variance is estimated from the results of each laboratory at each test site and is denoted by σ^2.

- *Laboratory bias* –The laboratory bias component measures the dispersion in determinations made of the same true value, μ, due to use of the method by separate laboratories. These differences can be ascribed to such factors as different analysts and instrumentation, and the variance, σ_L^2, is estimated by comparing the results obtained by different laboratories at each test site.

- *Between-laboratory* –The between-laboratory component is estimated from the within-laboratory and laboratory bias terms. The between-laboratory standard deviation is an estimate of the variation that can be expected between two single determinations made of the same true value, μ, by two laboratories working independently. The between-laboratory variance, σ_b^2, is defined as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2.$$

B. Experimental Design

The data were collected from three separate tests of Method 5 at three sources covered by the new source performance standards.[1] At each site, four collaborating laboratories were used, but the laboratories and collaborators varied from one test site to another. The number of sampling runs also varied from site to site.

The model chosen is a *nested* or *hierarchical* model[5] with three *factors*: sites, labs-within-sites, and repetitions-within-labs-within-sites or error. There were three sites; a cement plant, a power plant, and an incinerator.

The determinations from each of the laboratories are considered only within the particular site where they were made. For each laboratory during each run of the test, determination of the stack gas composition by Method 3 and moisture fraction determination by Method 5 were called for.

For the analysis of the particulate matter determination at both the power plant and the cement plant, one laboratory's results were excluded. At the cement plant, Lab 102 deviated from Method 5 in the laboratory analysis of the particulate matter. However, this had no bearing on either the Method 3 data or the moisture fraction data, and thus Lab 102's results are included in this study. At the power plant, Lab 201 was eliminated due to the probable development of leakage during some runs and filter contamination due to use of a low-melting ground joint lubricant. Since this would adversely affect the volumes of stack gas and liquid collected due to the introduction of ambient air into the train, their moisture fractions are not usable. The Method 3 data from Lab 201 are unaffected and are included in the analysis.

The schematic of the design for the treatment of the various Method 3 results is shown in Figure 1. The schematic design for the analysis of the moisture fraction data is shown in Figure 2. The number of repetitions, r_i, varies slightly

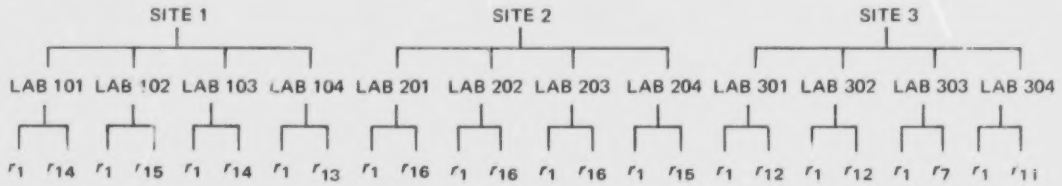

FIGURE 1. SCHEMATIC TEST PLAN, METHOD 3

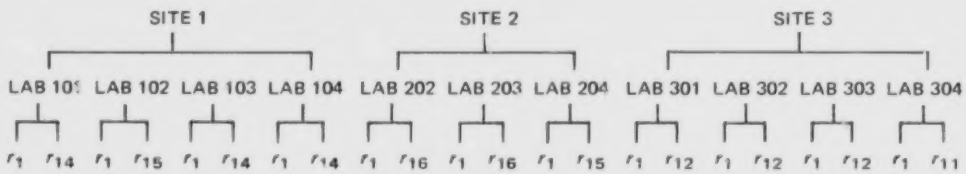

FIGURE 2. SCHEMATIC TEST PLAN, MOISTURE FRACTION

from lab to lab at each site due to a failure to complete the run, or in the case of Lab 303, failure to perform an Orsat analysis.

C. Data Handling and Analysis

The raw data from the tests were used to obtain the determination values used in the analysis. All Method 3 values shown were calculated using the three stack gas content determinations as a starting point, and the moisture fractions were calculated from the dry gas volume and volume of liquid collected.

Method 3 specifies that three consecutive analyses be made which differ by no more than 0.2 percent by volume for each of CO_2, O_2 and CO. This requirement was not enforced in the collaborative tests due to time and difficulty

factors. It has been demonstrated[7] that this requirement is stricter than can reasonably be expected by a qualified analyst using the specified equipment. Thus, the data as shown are the averages of three consecutive analyses on an integrated gas sample.

The *statistical model* for this experiment is of the form

$$Y_{ijk} = \mu + \gamma_i + \lambda_{j|i} + \epsilon_{k|j|i}$$

where

Y_{ijk} is the k^{th} repetition by lab j at site i.

μ is the overall mean.

γ_i is the effect of the i^{th} site.

$\lambda_{j|i}$ is the effect due to laboratory j at site i.

$\epsilon_{k|j|i}$ is the random error associated with Y_{ijk}.

The site factor is not of interest, since it merely reflects the differences in the levels of the parameters of interest from site to site. Its inclusion in the analysis serves as a restriction on the error term by removing these effects.

The lab factor, $\lambda_{j|i}$, provides an estimate of the laboratory bias variance by comparing the results from different laboratories at the same site. The error term, $\epsilon_{k|j|i}$, is the source of the within-laboratory variance, assumed constant, and comes from comparison of results by the same laboratory at the same site.

The sampling runs at each site are considered replicate determinations of the same true level for the various factors studied. This is done since the true levels were unknown, no independent means were available to measure them, and since inspection of the data does not indicate a great disparity in the level of any factor. As a result, the error term reflects both normal sampling error and fluctuation in the true level and is probably larger than the true within-laboratory variance. The laboratory bias term is essentially free from any error due to level fluctuation, since it is determined by comparing the averages of all the runs.

IV. METHOD 3

Method 3 is for the determination of CO_2, dry molecular weight, and percentage of excess air. The method calls for the use of an Orsat analyzer or equivalent to determine the CO_2, O_2, and CO content of the stack gas. All the analyses in this study were performed using Orsat equipment. At all sites tested, there was no detectable percentage of CO, and thus the resultant variables for study with regard to Method 3 were:

(1) $\%\ CO_2$.

(2) $\%\ O_2$.

(3) Dry Molecular Weight (*Md.*).

(4) Excess Air (*%EA*).

These variables were considered both with respect to the precision that can be expected in their determination and, where applicable, to the degree that their imprecision could affect the results of a performance test for compliance. The results of the statistical treatment are presented in the following sections, while more detail of the analyses is contained in the appropriate Appendix C section.

A. Carbon Dioxide

The CO_2 determinations made by the collaborators for the three test sites are shown in Table 1. These values were used in an Analysis of Variance (AOV) on the nested design to give the following results in terms of the precision associated with a single CO_2 determination by Method 3 using an Orsat analyzer. The precision estimates are obtained in Appendix C.2.

The within-laboratory variance estimate for the $\%\ CO_2$ determinations is

$$\delta^2 = 2.06$$

This estimate has 149 degrees of freedom associated with it. The estimated within-laboratory standard deviation is given by

$$\delta = \sqrt{\delta^2}$$

$$= \sqrt{2.06}$$

$$= 1.44\ \%\ CO_2$$

The laboratory bias variance, σ_L^2, is estimated as

$$\delta_L^2 = 1.12$$

with 9 degrees of freedom. The estimated laboratory bias standard deviation is

$$\delta_L = \sqrt{\delta_L^2}$$

$$= \sqrt{1.12}$$

$$= 1.06\ \%\ CO_2.$$

TABLE 1. CARBON DIOXIDE DATA
% CO_2 by volume

Run	Site 1			
	Labs			
	101	102	103	104
1	9.0	9.0	–*	2.9
2	7.4	9.0	9.0	7.2
3	6.0	9.0	9.2	5.1
4	7.0	7.0	11.4	8.3
5	7.0	10.4	9.1	4.0
6	10.0	10.5	9.1	10.0
7	4.6	4.0	5.4	4.6
8	4.6	7.2	5.8	–*
9	6.5	7.6	7.1	7.5
10	5.8	8.0	7.6	7.4
11	6.8	8.0	7.2	7.2
12	7.0	7.6	7.2	6.7
13	6.0	9.6	6.6	–*
14	–*	9.6	8.5	8.1
15	4.7	8.6	8.3	6.4

Run	Site 2			
	Labs			
	201	202	203	204
1	7.6	5.2	13.4	13.2
2	7.6	8.0	13.3	12.1
3	9.4	12.6	12.7	11.6
4	9.7	12.0	12.6	13.2
5	8.7	13.0	12.9	13.0
6	10.3	12.6	12.7	12.5
7	9.9	10.5	13.1	12.4
8	9.8	11.5	13.7	12.6
9	9.7	13.2	12.9	11.9
10	10.0	13.6	13.4	12.8
11	8.1	12.7	12.9	12.7
12	10.2	12.2	12.3	12.4
13	12.8	13.1	12.8	12.5
14	13.1	12.4	13.0	–*
15	11.7	10.6	13.4	13.0
16	12.4	10.2	13.1	12.6

Run	Site 3			
	Labs			
	301	302	303	304
1	6.4	4.8	4.8	–*
2	4.3	4.0	4.0	3.8
3	6.2	4.3	1.0	3.0
4	6.0	6.8	5.0	3.7
5	7.2	7.1	5.0	3.7
6	5.2	5.6	5.2	3.2
7	5.7	6.4	6.1	4.1
8	5.0	6.1	–†	5.4
9	5.1	6.6	–†	5.3
10	5.5	5.9	–†	4.3
11	6.1	7.9	–†	4.8
12	5.7	4.9	–†	3.0

*Run aborted, no Orsat data taken.
†No analyses made.

Combining the previous estimates, the between-laboratory variance, σ_b^2, is estimated as

$$\delta_b^2 = \delta_L^2 + \delta^2$$

$$= 2.06 + 1.12$$

$$= 3.18.$$

This gives an estimated between-laboratory standard deviation of

$$\delta_b = \sqrt{3.18}$$

$$= 1.78 \% CO_2$$

The percent CO_2 determination is used as a correction factor in the determination of particulate emissions from incinerators according to the formula

$$k = \frac{12}{\% CO_2}.$$

The effect of a deviation from the actual % CO_2 upon this correction factor and upon the particulate concentration determination can be demonstrated by considering the case where the determined value differs from the actual by one standard deviation. The between-laboratory standard deviation is used since this gives an indication of the comparative results of two independent testing facilities working at the same true particulate concentration and CO_2 level. Let,

V_i be the corrected concentration value for lab i

C be the uncorrected concentration

k_i be the correction factor determined by lab i.

Then

$$V_i = k_i C.$$

Suppose that one laboratory determines the correct CO_2 percent and the other differs by one between-laboratory standard deviation. Then the factors are

$$k_1 = \frac{12}{\% CO_2}$$

$$k_2 = \frac{12}{\% CO_2 \pm \sigma_b},$$

and the concentrations are reported as

$$V_1 = \left(\frac{12}{\% CO_2}\right) C$$

$$V_2 = \left(\frac{12}{\%\,CO_2 \pm \sigma_b}\right)C$$

The error that would be induced by a one standard deviation error can be shown by taking the ratio of the two concentration values, V_1 / V_2.

$$\frac{V_1}{V_2} = \frac{\dfrac{12}{\%\,CO_2}\,C}{\dfrac{12}{\%\,CO_2 \pm \sigma_b}\,C}$$

$$= \frac{12C}{\%\,CO_2} \cdot \frac{\%\,CO_2 \pm \sigma_b}{12C}$$

$$= \frac{\%\,CO_2 \pm \sigma_b}{\%\,CO_2}.$$

Assuming true values of 5, 8, and 11 percent for $\%\,CO_2$, the resultant error can be demonstrated. For 5 percent, one standard deviation high gives

$$\frac{V_1}{V_2} = \frac{5\% + 1.78\%}{5\%}$$

$$= \frac{6.78}{5}$$

$$= 1.36.$$

One standard deviation low gives

$$\frac{V_1}{V_2} = \frac{5\% - 1.78\%}{5\%}$$

$$= \frac{3.22}{5}$$

$$= 0.64.$$

Similarly, for true values of 8 and 11 percent the ratios are 1.22 and 0.78, and 1.16 and 0.84, respectively. Thus, the data from these tests indicate that variation of one standard deviation in the CO_2 level would cause the reported particulate concentrations of two laboratories to differ by 36 percent at low CO_2 levels, and 16 percent at high CO_2 levels, when corrected to 12% CO_2.

B. Oxygen

The percentage of oxygen in the stack gas is also measured by the Orsat analyzer. There is no direct application of this to a standard of performance, but it is used in the computation of both the dry molecular weight of the gas stream and the percentage of excess air. The O_2 determinations from the three sites are presented in Table 2.

TABLE 2. OXYGEN DETERMINATION DATA
% O_2 by volume

Run	Site 1			
	Labs			
	101	102	103	104
1	12.0	12.2	–*	16.8
2	13.6	12.2	15.4	6.1
3	14.2	12.8	11.5	16.5
4	13.7	14.8	10.6	13.4
5	13.7	11.4	11.7	17.8
6	10.7	11.5	11.4	11.2
7	16.2	17.0	16.0	16.2
8	16.2	14.4	14.2	–*
9	13.2	14.0	13.0	13.8
10	14.1	14.0	13.6	12.7
11	13.9	13.2	13.4	13.9
12	13.7	14.0	13.8	14.5
13	14.2	12.2	14.2	–*
14	–*	12.6	12.3	13.0
15	14.7	13.0	12.3	14.8

Run	Site 2			
	Labs			
	201	202	203	204
1	8.1	14.3	4.6	4.8
2	8.1	11.4	5.0	6.4
3	8.2	5.3	5.5	6.4
4	8.2	6.7	5.9	5.2
5	9.3	5.2	5.3	5.0
6	7.3	6.2	5.4	6.0
7	8.0	7.0	5.0	5.8
8	8.1	6.1	4.6	5.9
9	8.0	5.1	5.5	6.4
10	7.8	4.9	5.4	5.6
11	9.0	5.8	5.0	5.8
12	7.0	6.3	6.0	6.2
13	4.3	6.3	6.0	5.8
14	4.8	6.5	5.0	–*
15	4.7	7.3	5.0	5.5
16	4.2	8.2	5.0	5.8

Run	Site 3			
	Labs			
	301	302	303	304
1	14.0	14.2	15.0	–*
2	15.3	14.0	11.5	15.7
3	13.7	13.4	20.0	16.7
4	13.7	10.8	15.0	20.0
5	13.5	10.3	15.0	17.0
6	14.7	11.0	14.9	16.8
7	14.1	10.3	14.1	16.7
8	14.5	10.0	–†	14.8
9	14.6	10.3	–†	14.1
10	14.3	10.2	–†	15.3
11	13.8	8.6	–†	16.6
12	14.2	10.2	–†	17.5

*Run not made.
†Orsat data not taken.

In Appendix C.3, the AOV table is shown for these determinations and the appropriate variance components estimated. Under the assumption that the O_2 level remained essentially constant over the testing period, we can estimate a within-laboratory variance, σ^2, of

$$\hat{\sigma}^2 = 2.90$$

with 149 degrees of freedom. This gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{2.90}$$

$$= 1.70\% \text{ } O_2 \text{ by volume.}$$

From the laboratory factor of the analysis, the laboratory bias variance, σ_L^2, may be estimated as

$$\hat{\sigma}_L^2 = 1.66$$

with 9 degrees of freedom. Then the estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_L^2}$$

$$= \sqrt{1.66}$$

$$= 1.29\% \text{ } O_2 \text{ by volume.}$$

Combining the above components, we can estimate a between-laboratory variance, σ_b^2, by the formula in section IIIA. The estimated value is

$$\hat{\sigma}_b^2 = \hat{\sigma}_L^2 + \hat{\sigma}^2$$

$$\hat{\sigma}_b^2 = (1.66) + (2.90)$$

$$= 4.56$$

Then the between-laboratory standard deviation is estimated by

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= \sqrt{4.56}$$

$$= 2.14\% \text{ } O_2 \text{ by volume.}$$

Thus, the between-laboratory standard deviations for both CO_2 and O_2 are in fairly close agreement. This is consistent with comments made by users of the Orsat method that there is a trade-off between CO_2 and O_2. That is, a loss of CO_2 results in an equivalent gain in O_2.

TABLE 3. DRY MOLECULAR WEIGHT DATA
lb/lb-mole

Run	Site 1			
	Labs			
	101	102	103	104
1	29.92	29.93	*	29.14
2	30.01	29.93	30.06	29.40
3	29.53	29.95	29.93	29.48
4	29.67	29.71	30.53	29.86
5	20.67	30.12	29.92	29.35
6	30.03	30.14	29.91	30.05
7	29.38	29.32	29.50	29.38
8	29.38	29.73	29.22	*
9	29.57	29.78	29.38	29.75
10	29.49	29.84	29.76	29.41
11	29.64	29.81	29.69	29.71
12	29.67	29.78	29.70	29.65
13	29.53	30.02	29.62	-*
14	-	30.15	29.85	29.82
15	29.34	29.90	29.82	29.62

Run	Site 2			
	Labs			
	201	202	203	204
1	29.54	29.40	30.33	30.30
2	29.54	29.74	30.33	30.19
3	29.83	30.23	30.25	30.11
4	29.96	30.19	30.25	30.04
5	29.76	30.29	30.28	30.28
6	29.94	30.26	30.25	30.24
7	29.90	29.96	30.30	30.22
8	29.89	30.08	30.38	30.25
9	29.87	30.32	30.28	30.16
10	29.91	30.37	30.36	30.27
11	29.66	30.26	30.26	30.26
12	29.91	30.20	30.21	30.23
13	30.22	30.35	30.29	30.23
14	30.29	30.24	30.28	-
15	30.06	29.99	30.34	30.30
16	30.15	29.96	30.30	30.25

Run	Site 3			
	Labs			
	301	302	303	304
1	29.58	29.34	29.65	-
2	29.30	29.20	29.10	29
3	29.54	29.22	28.96	29.24
4	29.51	29.52	29.40	29.15
5	29.69	29.27	29.40	29.27
6	29.48	29.34	29.43	29.18
7	29.48	29.44	29.54	29.32
8	29.38	29.38	-†	29.46
9	29.40	29.47	-†	29.41
10	29.45	29.35	-†	29.30
11	29.53	29.61	-†	29.43
12	29.48	29.19	-†	29.18

*Run not made.
†No Orsat data taken.

Note: EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report, the factor is:

1 lb/lb-mole ≈ 1 gm/gm-mole.

C. Dry Molecular Weight

The dry molecular weight (*Md*) of the stack gas is determined from the stack gas analysis. The formula is

$$Md = (0.44)\,\%\,CO_2 + (0.32)\,\%\,O_2 + (0.28)(\%\,N_2 + \%\,CO).$$

The sites tested had no detectable CO, and since the percent N_2 is determined by subtraction, the values for *Md* used in this report depend solely on the CO_2 and O_2 determinations. Thus, in this section the precision of the *Md* determination is given, along with the relationship of that precision to the precision of the CO_2 and O_2 determinations.

The dry molecular weights used in the analysis are shown in Table 3. Submitting these to an AOV according to the model discussed gives the precision estimates desired. The values are obtained in Appendix C.4.

The within-laboratory variance, σ^2, is estimated as

$$\hat{\sigma}^2 = 0.04$$

with 149 degrees of freedom. From this, the estimated within-laboratory standard deviation is

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{0.04}$$

$$= 0.2 \text{ lb/lb-mole.}$$

The estimated laboratory bias variance is

$$\hat{\sigma}_L^2 = 0.02$$

with 9 degrees of freedom. Thus, the estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \sqrt{0.02}$$

$$= 0.14 \text{ lb/lb-mole.}$$

Combining estimates, the between-laboratory variance, σ_b^2, for the determination of dry molecular weight is estimated as

$$\hat{\sigma}_b^2 = \hat{\sigma}_L^2 + \hat{\sigma}^2$$

$$= (0.02) + (0.04)$$

$$= 0.06,$$

and the estimated between-laboratory standard deviation is

$$\hat{\sigma}_b = \sqrt{0.06}$$

$$= 0.24 \text{ lb/lb-mole.}$$

TABLE 4. PERCENT EXCESS AIR DATA

Run	Site 1			
	Labs			
	101	102	103	104
1	135.5	141.8	–*	381.9
2	180.9	141.8	337.8	36.3
3	206.8	163.2	121.9	393.1
4	189.4	253.2	103.4	184.3
5	189.4	123.3	127.1	625.7
6	104.5	126.5	118.9	116.6
7	344.0	440.9	336.8	344.0
8	344.0	228.7	213.3	–*
9	165.0	209.0	166.0	197.8
10	200.1	212.4	188.8	156.2
11	197.6	173.6	177.2	200.6
12	189.4	209.0	195.6	230.0
13	206.8	144.5	211.7	–*
14	–*	156.6	142.9	166.0
15	223.5	168.9	142.0	246.5

Run	Site 2			
	Labs			
	201	202	203	204
1	57.2	205.7	27.0	28.5
2	57.2	115.4	30.2	42.3
3	60.5	32.4	34.2	42.0
4	60.9	45.4	37.8	32.3
5	75.3	31.7	32.5	30.0
6	50.5	40.7	33.3	38.7
7	58.5	47.4	30.1	36.7
8	59.7	39.0	27.1	37.8
9	58.3	31.0	34.3	42.2
10	56.1	29.5	33.7	35.1
11	69.8	36.9	30.0	36.9
12	47.1	41.4	38.5	40.6
13	24.5	42.1	38.9	36.8
14	28.4	43.6	30.0	–*
15	27.1	50.8	30.0	34.3
16	23.6	61.5	30.1	36.8

Run	Site 3			
	Labs			
	301	302	303	304
1	199.6	197.7	233.0	–
2	258.2	183.1	106.4	282.8
3	184.0	160.9	2336.4	371.2
4	182.7	98.6	245.1	13966.5
5	181.6	91.6	245.1	432.0
6	226.2	99.8	240.6	388.9
7	199.4	88.1	202.4	396.8
8	214.8	82.3	–†	236.2
9	221.2	88.5	–†	196.4
10	208.1	85.4	–†	258.2
11	187.8	64.0	–†	400.0
12	204.4	83.5	–†	501.7

*Runs not made.
†No Orsat data taken.

Thus, there is little variation in the computed dry molecular weights, especially in light of the variation demonstrated previously for the CO_2 and O_2 determinations. This has been noted in other studies on the Orsat method.[7] The trade-off between CO_2 and O_2 mentioned earlier is responsible for this small deviation in *Md*. If we assume a loss of 2% CO_2 by volume and a resultant gain of 2% O_2 by volume, the net effect on *Md* would be:

$$Md = (0.44)(\%\,CO_2 - 2\%) + (0.32)(\%\,O_2 + 2\%) + (0.28)(\%\,N_2 + \%\,CO)$$

$$= (0.44)(\%\,CO_2) - (0.44)(2\%) + (0.32)(\%O_2) + (0.32)(2\%) + (0.28)(\%\,N_2 + \%\,CO)$$

$$= (0.44)(\%CO_2) + (0.32)(\%O_2) + (0.28)(\%N_2 + \%\,CO) + (0.32)(2\%) - (0.44)(2\%)$$

$$= \text{dry molecular weight} + (0.32 - 0.44)\,2\%$$

$$= \text{dry molecular weight} - 0.24.$$

The result would be an estimate that fell 0.24 below the actual value. A comparison of the between-laboratory standard deviations for CO_2, O_2 and *Md* gives credence to this trade-off explanation.

D. Excess Air

The excess air percentage is determined according to the formula

$$\%\,EA = \frac{(\%\,O_2) - 0.5\,(\%\,CO)}{(0.264)(\%\,N_2) - (\%\,O_2) + (0.5)(\%\,CO)} \times 100 \text{ percent}$$

Using the data from Tables 1 and 2, the excess air determinations were computed, and the values are shown in Table 4.

It is apparent from the data that there is a great deal of imprecision in this computation. Rather than apply an AOV approach to obtain precision estimates, the factor or factors upon which the *% EA* determination depends is investigated. In the absence of CO, the above formula can be expressed as

$$\%\,EA = \frac{\%\,O_2}{(0.264)(\%\,N_2) - \%\,O_2} \times 100 \text{ percent}$$

and since $\%N_2 = 100 - \%\,O_2 - \%\,CO_2$,

$$\%\,EA = \frac{\%\,O_2}{(0.264)(100 - \%\,O_2 - \%\,CO_2) - \%\,O_2} \times 100 \text{ percent}$$

$$= \frac{\%\,O_2}{26.4 - (1.264)\%\,O_2 - (0.264)\%\,CO_2} \times 100 \text{ percent.}$$

Thus, the excess air is the ratio of the oxygen content to a constant less a percentage of the O_2 and CO_2 fractions. But since only about one-quarter of the % CO_2 is involved in the denominator, this amounts usually to a relatively small contribution to the overall determination. As a result, the factor making the significant contribution to the estimate is the oxygen percentage.

Based upon this and the nature of the data, an exponential model for the excess air was proposed as

$$y = a_0 e^{a_1 x}$$

where

y is % EA

x is % O_2

e is the base of the natural logarithms

and

a_0, a_1 are constants.

A least squares fit of a sample of the excess air determinations taken from all three sites was used to estimate a_0 and a_1 and to determine the degree of fit. The steps used are shown in Appendix C.5. The model obtained was

$$y = (10.47)e^{(0.21)x}.$$

The degree of fit, as measured by the coefficient of determination, r^2, is

$$r^2 = 0.993$$

indicating an extreme closeness of the determinations to the model.

By using this model and the previously determined precision estimate for % O_2 determination, it is possible to demonstrate the imprecision of the excess air determination. Using the between-laboratory standard deviation of 2.14% O_2, we can estimate the effect on the excess air determination of an error of one standard deviation in the O_2 determination.

If we let x = % O_2 be the actual percentage of O_2 in the gas, and y be the actual percentage of excess air, then a standard deviation of 2.14% O_2 implies

$$y_c = (10.47)e^{(0.21)(x + 2.14)}$$

where y_c is the calculated excess air. Then

$$y_c = (10.47)e^{(0.21)x + (0.21)(2.14)}$$

$$= [(10.47)e^{(0.21)x}]\, e^{(0.21)(2.14)}$$

$$= y \cdot e^{(0.45)}$$

$$= (1.57)y.$$

Thus a normal error in O_2 determination would result in a 57% error in the excess air determination. Similarly, a one standard deviation error in the negative direction implies

$$y_c = \frac{1}{1.57} y$$

$$= (0.64)y$$

From the above, it can be seen that the excess air determination can only be as reliable as the O_2 determination, and due to the exponential relationship, small deviations in O_2 result in large deviations in excess air.

V. MOISTURE FRACTION

The moisture fractions for this study were obtained using the formula given in Method 5. The equation is

$$B_{wo} = \frac{V_{w_{std}}}{V_{w_{std}} + V_{m_{std}}}$$

where

$V_{w_{std}}$ – the volume of water vapor collected, corrected to standard conditions.

$V_{m_{std}}$ – the volume of gas collected, dry basis, corrected to standard conditions.

The water vapor collected is determined by adding the water volume increase in the impingers to the weight increase in the silica gel tube in grams, and multiplying by a constant factor. Using the above formula, the moisture fractions used in the analysis were obtained, and these are shown in Table 5.

The precision estimates for the moisture fraction determination are obtained using an AOV in the design that was shown in Figure 2. The AOV table and related data are shown in Appendix C.6.

The within-laboratory variance, σ^2, is estimated as

$$\hat{\sigma}^2 = 0.001$$

with 140 degrees of freedom. This gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= 0.032$$

The laboratory bias variance estimate obtained was

$$\hat{\sigma}_L^2 = 0.001$$

with 8 degrees of freedom. The laboratory bias standard deviation, then, is given by

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_L^2}$$

$$= 0.032$$

Using the above values, the estimated between-laboratory variance is

$$\hat{\sigma}_b^2 = \hat{\sigma}_L^2 + \hat{\sigma}^2$$

$$= (0.001) + (0.001)$$

$$= 0.002.$$

and the between-laboratory standard deviation is estimated as

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= 0.045$$

TABLE 5. MOISTURE FRACTION DATA

Run	Site 1			
	Labs			
	101	102	103	104
1	0.26	0.33	–*	0.28
2	0.30	0.31	0.19	0.27
3	0.30	0.33	0.24	0.23
4	0.32	0.30	0.27	0.30
5	0.31	0.38	0.28	0.32
6	0.31	0.32	0.26	0.30
7	0.20	0.21	0.21	0.16
8	0.22	0.23	0.22	0.22
9	[illegible]	0.26	0.18	0.25
10	0.23	0.26	0.22	0.24
11	0.25	0.28	0.23	0.28
12	0.26	0.26	0.21	0.28
13	0.26	0.28	0.22	–*
14	–*	0.30	0.24	0.29
15	0.26	0.28	0.23	0.28

Run	Site 2		
	Labs		
	202	203	204
1	0.10	0.05	0.10
2	0.10	0.09	0.08
3	0.10	0.09	0.09
4	0.10	0.10	0.10
5	0.11	0.09	0.10
6	0.10	0.10	0.10
7	0.11	0.08	0.10
8	0.10	0.09	0.10
9	0.10	0.09	0.09
10	0.10	0.09	0.09
11	0.11	0.10	0.11
12	0.11	0.09	0.10
13	0.10	0.09	0.10
14	0.10	0.10	–*
15	0.11	0.10	0.10
16	0.10	0.10	0.10

Run	Site 3			
	Labs			
	301	302	303	304
1	0.37	0.29	0.37	–*
2	0.37	0.27	0.43	0.40
3	0.30	0.30	0.41	0.40
4	0.38	0.32	0.44	0.23
5	0.42	0.33	0.44	0.32
6	0.35	0.29	0.40	0.37
7	0.37	0.32	0.41	0.40
8	0.38	0.31	0.38	0.42
9	0.35	0.32	0.43	0.43
10	0.32	0.29	0.41	0.40
11	0.35	0.32	0.43	0.42
12	0.38	0.28	0.39	0.36

*Runs not made.

APPENDIX A

METHOD 3. GAS ANALYSIS FOR CARBON DIOXIDE, EXCESS AIR, AND DRY MOLECULAR WEIGHT.

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. *Principle and applicability.*

1.1 Principle. An integrated or grab gas sample is extracted from a sampling point and analyzed for its components using an Orsat analyzer.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the New Source Performance Standards. The test procedure will indicate whether a grab sample or an integrated sample is to be used.

2. *Apparatus.*

2.1 Grab sample (Figure 3-1).

2.1.1 Probe—Stainless steel or Pyrex[1] glass, equipped with a filter to remove particulate matter.

2.1.2 Pump—One-way squeeze bulb, or equivalent, to transport gas sample to analyzer.

[1] Trade name.

2.2 *Integrated sample (Figure 3-2).*

2.2.1 Probe—Stainless steel or Pyrex[1] glass, equipped with a filter to remove particulate matter.

2.2.2 Air-cooled condenser or equivalent—To remove any excess moisture.

2.2.3 Needle valve—To adjust flow rate.

2.2.4 Pump—Leak-free, diaphragm type, or equivalent, to pull gas.

2.2.5 Rate meter—To measure a flow range from 0 to 0.035 cfm.

2.2.6 Flexible bag—Tedlar,[1] or equivalent, with a capacity of 2 to 3 cu. ft. Leak test the bag in the laboratory before using.

2.2.7 Pitot tube—Type S, or equivalent, attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

2.3 *Analysis.*

2.3.1 Orsat analyzer, or equivalent.

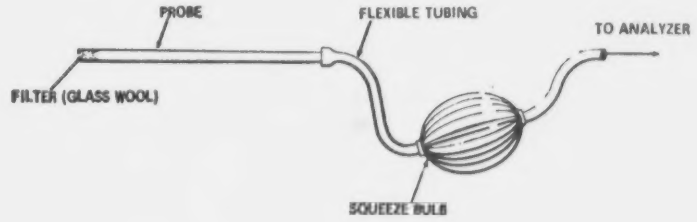

Figure 3-1. Grab-sampling train.

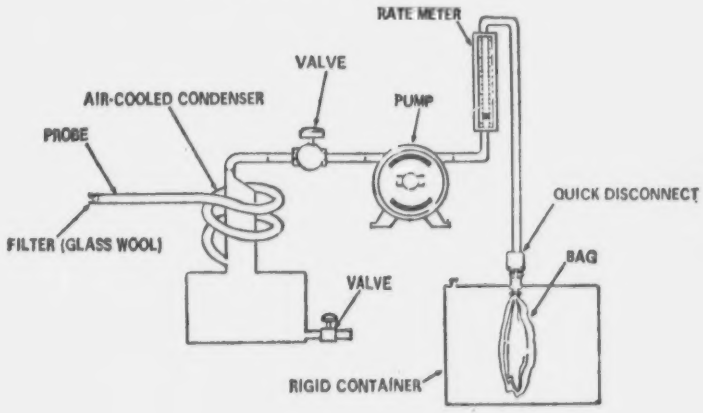

Figure 3-2. Integrated gas-sampling train.

3. *Procedure.*

3.1 Grab sampling.

3.1.1 Set up the equipment as shown in Figure 3-1, making sure all connections are leak-free. Place the probe in the stack at a sampling point and purge the sampling line.

3.1.2 Draw sample into the analyzer.

3.2 Integrated sampling.

3.2.1 Evacuate the flexible bag. Set up the equipment as shown in Figure 3-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are tight and that there are no leaks.

3.2.2 Sample at a rate proportional to the stack velocity.

3.3 Analysis.

3.3.1 Determine the CO_2, O_2, and CO concentrations as soon as possible. Make as many passes as are necessary to give constant readings. If more than ten passes are necessary, replace the absorbing solution.

3.3.2 For grab sampling, repeat the sampling and analysis until three consecutive samples vary no more than 0.5 percent by volume for each component being analyzed.

3.3.3 For integrated sampling, repeat the analysis of the sample until three consecutive analyses vary no more than 0.2 percent by volume for each component being analyzed.

4. *Calculations.*

4.1 Carbon dioxide. Average the three consecutive runs and report the result to the nearest 0.1% CO_2.

4.2 Excess air. Use Equation 3-1 to calculate excess air, and average the runs. Report the result to the nearest 0.1% excess air.

$$\%\,EA = \frac{(\%\,O_2) - 0.5(\%\,CO)}{0.264(\%\,N_2) - (\%\,O_2) + 0.5(\%\,CO)} \times 100 \qquad \text{equation 3-1}$$

where:

%EA = Percent excess air.
$\%\,O_2$ = Percent oxygen by volume, dry basis.
$\%\,N_2$ = Percent nitrogen by volume, dry basis.
%CO = Percent carbon monoxide by volume, dry basis.
0.264 = Ratio of oxygen to nitrogen in air by volume.

4.3 Dry molecular weight. Use Equation 3-2 to calculate dry molecular weight and average the runs. Report the result to the nearest tenth.

$$M_d = 0.44(\%\,CO_2) + 0.32(\%\,O_2) + 0.28(\%\,N_2 + \%\,CO) \qquad \text{equation 3-2}$$

where:

M_d = Dry molecular weight, lb./lb-mole.
$\%\,CO_2$ = Percent carbon dioxide by volume, dry basis.
$\%\,O_2$ = Percent oxygen by volume, dry basis.
$\%\,N_2$ = Percent nitrogen by volume, dry basis.
0.44 = Molecular weight of carbon dioxide divided by 100.
0.32 = Molecular weight of oxygen divided by 100.
0.28 = Molecular weight of nitrogen and CO divided by 100.

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5. *References.*

Altshuller, A. P., et al., Storage of Gases and Vapors in Plastic Bags, Int. J. Air & Water Pollution, 6:75–81, 1963.

Conner, William D., and J. S. Nader, Air Sampling with Plastic Bags, Journal of the American Industrial Hygiene Association, 25:291–297, May–June 1964.

Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

METHOD 4—DETERMINATION OF MOISTURE IN STACK GASES

1. *Principle and applicability.*

1.1 Principle. Moisture is removed from the gas stream, condensed, and determined volumetrically.

1.2 Applicability. This method is applicable for the determination of moisture in stack gas only when specified by test procedures for determining compliance with New Source Performance Standards. This method does not apply when liquid droplets are present in the gas stream[1] and the moisture is subsequently used in the determination of stack gas molecular weight.

Other methods such as drying tubes, wet bulb-dry bulb techniques, and volumetric condenser techniques may be used.

2. *Apparatus.*

2.1 Probe—Stainless steel or Pyrex[2] glass sufficiently heated to prevent condensation and equipped with a filter to remove particulate matter.

2.2 Impingers—Two midget impingers, each with 30 ml. capacity, or equivalent.

2.3 Ice bath container—To condense moisture in impingers.

2.4 Silica gel tube (optional)—To protect pump and dry gas meter.

2.5 Needle valve—To regulate gas flow rate.

2.6 Pump—Leak-free, diaphragm type, or equivalent, to pull gas through train.

2.7 Dry gas meter—To measure to within 1%, of the total sample volume.

2.8 Rotameter—To measure a flow range from 0 to 0.1 c.f.m.

2.9 Graduated cylinder—25 ml.

2.10 Barometer—Sufficient to read to within 0.1 inch Hg.

2.11 Pitot tube—Type S, or equivalent, attached to probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

3. *Procedure.*

3.1 Place exactly 5 ml. distilled water in each impinger. Assemble the apparatus without the probe as shown in Figure 4-1. Leak check by plugging the inlet to the first impinger and drawing a vacuum. Insure that flow through the dry gas meter is less than 1% of the sampling rate.

3.2 Connect the probe and sample at a constant rate of 0.075 c.f.m. or at a rate proportional to the stack gas velocity. Continue sampling until the dry gas meter registers 1 cubic foot or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-2.

3.3 After collecting the sample, measure the volume increase to the nearest 0.5 ml.

4. *Calculations.*

4.1 Volume of water vapor collected.

$$V_{ws}=\frac{(V_f-V_i)\rho_{w,a}RT_{std}}{P_{std}M_{H_2O}}=0.0474\frac{ft.^3}{ml.}(V_f-V_i) \qquad \text{equation 4-1}$$

where:

V_{ws} = Volume of water vapor collected (standard conditions), cu. ft.

V_f = Final volume of impinger contents, ml.

V_i = Initial volume of impinger contents, ml.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb mole-°R.

$\rho_{w,a}$ = Density of water, 1 g./ml.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

M_{H_2O} = Molecular weight of water, 18 lb./lb-mole.

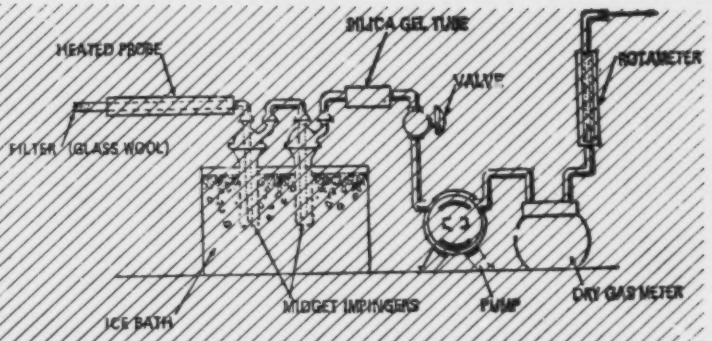


Figure 4-1. Moisture-sampling train.

LOCATION _____ COMMENTS

TEST _____

DATE _____

OPERATOR _____

BAROMETRIC PRESSURE _____

CLOCK TIME	GAS VOLUME THROUGH METER, (V_m), ft^3	ROTAMETER SETTING ft^3/min	METER TEMPERATURE, °F

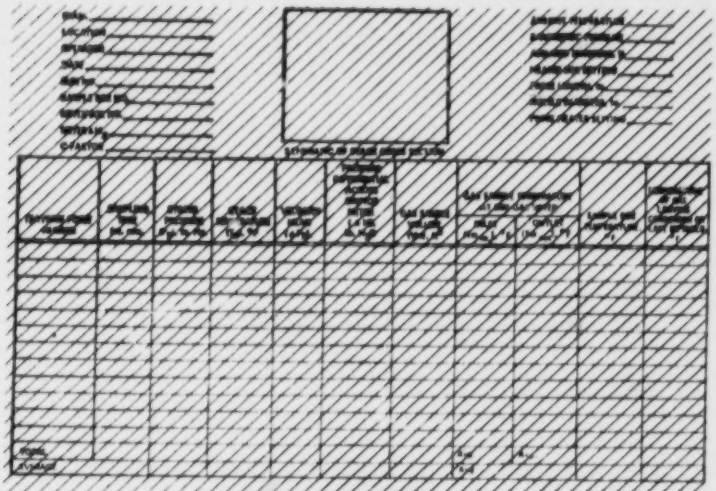
Figure 4-2. Field moisture determination.

[1] If liquid droplets are present in the gas stream, assume the stream to be saturated, determine the average stack gas temperature by traversing according to Method 1, and use a psychrometric chart to obtain an approximation of the moisture percentage.

[2] Trade name.

APPENDIX B

MOISTURE FRACTION DETERMINATION FROM METHOD 5



4 sheets per test run

6.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to loosen adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

6.3 Analysis. Record the data required on the example sheet shown in Figure 5-2. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration.*

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations.*

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F, 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\ \frac{°R}{in.\ Hg}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho_{H_2O}}{M_{H_2O}}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474\ \frac{cu.\ ft.}{ml.}\right)V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρ_{H_2O} = Density of water, 1 g/ml.

M_{H_2O} = Molecular weight of water, 18 lb/lb-mole.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{w_s} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{w_s} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-2).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154\ \frac{gr.}{mg.}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, dry basis, gr./s.c.f.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

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PLANT_____

DATE _____

RUN NO._____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g/ml):

$$\frac{\text{INCREASE, g}}{\text{(1 g/ml)}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb/cu. ft.

$$c_s = \left(\frac{\text{lb}}{453,600\ \text{mg}}\right) M_n \frac{}{V_{m_{std}}} = 2.205 \times 10^{-6} \frac{M_n}{V_{m_{std}}} \qquad \text{equation 5-5}$$

where:

c_s = Concentration of particulate matter in lb/cu. ft. dry gas at standard conditions.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \left[\frac{V_{lc}(\rho_w/\rho_{lc}) + V_m\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{\theta A_n P_s}\right] \times 100$$

$$= \left(\frac{1\ \text{min}}{60\ \text{sec}}\right)\left(\frac{100\ \text{cm}}{\text{m}}\right)^3 \left(\frac{0.3048\ \text{m}}{\text{ft}}\right)^2 \left(\frac{\text{lb-mole}}{\text{lb}}\right) \left(\frac{\text{in. Hg}}{\text{mm Hg}}\right) \left(\frac{\text{mm Hg}}{\text{in. H}_2\text{O}}\right) \left(\frac{\text{ml}}{\text{cc}}\right) \left(\frac{\text{g}}{\text{ml}}\right) \left(\frac{\text{lb}}{\text{g}}\right) \left(\frac{\text{sec}}{\text{hr}}\right) \left(\frac{\text{K}}{^\circ\text{R}}\right) \left(\frac{\text{ft}^3}{\text{cu. ft.}}\right) \left(\frac{\text{sq. ft.}}{\text{sq. in.}}\right) \left(\frac{\text{sq. in.}}{\text{sq. cm}}\right) \left(\frac{\text{cu. ft.}}{\text{cu. m}}\right) \left(\frac{\text{cu. m}}{\text{cu. cm}}\right)$$

$$= \left[\frac{V_{lc}(\rho_w/\rho_{lc}) + V_m\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{\theta A_n P_s}\right] \times 100$$

$$= \left(\frac{1\ \text{min}}{60\ \text{sec}}\right)\left(\frac{100\ \text{cm}}{\text{m}}\right)^3 \left(\frac{0.3048\ \text{m}}{\text{ft}}\right)^2 \left(\frac{\text{lb-mole}}{\text{lb}}\right) \left(\frac{\text{in. Hg}}{\text{mm Hg}}\right) \left(\frac{\text{mm Hg}}{\text{in. H}_2\text{O}}\right) \left(\frac{\text{ml}}{\text{cc}}\right) \left(\frac{\text{g}}{\text{ml}}\right) \left(\frac{\text{lb}}{\text{g}}\right) \left(\frac{\text{sec}}{\text{hr}}\right) \left(\frac{\text{K}}{^\circ\text{R}}\right) \left(\frac{\text{ft}^3}{\text{cu. ft.}}\right) \left(\frac{\text{sq. ft.}}{\text{sq. in.}}\right) \left(\frac{\text{sq. in.}}{\text{sq. cm}}\right) \left(\frac{\text{cu. ft.}}{\text{cu. m}}\right) \left(\frac{\text{cu. m}}{\text{cu. cm}}\right)$$

$$\left(\frac{1\ \text{min}}{\text{sec}}\right)\left(\frac{\text{in. Hg}}{\text{mm Hg}}\right)\left(\frac{\text{mm Hg}}{\text{in. H}_2\text{O}}\right)\left(\frac{\text{ml}}{\text{cc}}\right)\left(\frac{\text{g}}{\text{ml}}\right)\left(\frac{\text{lb}}{\text{g}}\right)\left(\frac{\text{sec}}{\text{hr}}\right)\left(\frac{\text{K}}{^\circ\text{R}}\right)\left(\frac{\text{ft}^3}{\text{cu. ft.}}\right)\left(\frac{\text{sq. ft.}}{\text{sq. in.}}\right)\left(\frac{\text{sq. in.}}{\text{sq. cm}}\right)\left(\frac{\text{cu. ft.}}{\text{cu. m}}\right)\left(\frac{\text{cu. m}}{\text{cu. cm}}\right)$$

Equation 5-6

where:

I = Percent of isokinetic sampling.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Eq. 5-3), ml.

ρ_w = Density of water, 1 g/ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb-mole-°R.

M_w = Molecular weight of water, 18.0 lb/lb-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-3), °R.

P_{bar} = Barometric pressure at sampling site, in. Hg.

ΔH = Average pressure drop across the orifice (see Eq. 5-2), inches H$_2$O.

P_s = Absolute average stack gas temperature (see Eq. 5-2), °R.

θ = Total sampling time, min.

A_n = Stack cross-sectional area, sq. ft.

P_s = Absolute stack gas pressure, inches Hg.

M_d = Dry molecular weight of gas, lb/lb-mole.

6.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results.

If $90\% \leq I \leq 110\%$, the results are acceptable. Otherwise, reject the results and repeat the test.

7. References.

Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

Rom, Jerome J., Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

Method 6—Determination of sulfur dioxide emissions from stationary sources

1. Principle and applicability.

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The acid mist, including sulfur trioxide, is separated from the sulfur dioxide. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. Apparatus.

2.1 Sampling. See Figure 6-1.

2.1.1 Probe—Pyrex[1] glass, approximately 6 to 9 mm. ID, with a heating system to prevent condensation and a filtering medium to remove particulate matter including sulfuric acid mist.

2.1.2 Midget bubbler—One, with glass wool packed in top to prevent sulfuric acid mist carryover.

2.1.3 Glass wool.

2.1.4 Midget impingers—Three.

2.1.5 Drying tube—Packed with 6 to 16 mesh indicating-type silica gel, or equivalent, to dry the sample.

2.1.6 Valve—Needle valve, or equivalent, to adjust flow rate.

2.1.7 Pump—Leak-free vacuum type.

2.1.8 Pitot meter—Manometer or equivalent, to measure a 0-10 in. H$_2$O flow range.

2.1.9 Dry gas meter—Sufficiently accurate to measure the sample volume within 1%.

2.1.10 Pitot line—Type S, or equivalent.

[1] Trade name.

APPENDIX C. STATISTICAL METHODS

This appendix consists of various sections which contain details of statistical procedures carried out in the analysis of the data. Reference to these sections has been made at various junctures in the body of the report. Each section is an independent analysis pertinent to a particular portion of the report.

C.1 Expected Mean Squares

In an analysis of variance, the mean square for each factor is computed. The mean squares are variance estimates, and they are used to determine which factors affect the overall mean level. However, if the expected values of these variance estimates or expected mean squares are known, the individual variance components of interest can also be estimated.

The basic design used in this study is a nested design with unequal levels of the various factors. That is, the number of labs per site and repetitions per lab vary from one site to the next. The expected mean squares for this design are not determined in a straightforward manner, but rather they are obtained as a weighted average of the varying sample sizes. The F-tests obtained using these expected mean squares are inexact with the exception of the lowest order comparison made with respect to the error term. However, that is the only test of interest in this study.

The expected mean square (*EMS*) for the labs/sites factor consists of a within-laboratory term, σ^2, and a multiple of the laboratory bias term, σ_L^2. What is needed is to determine the multiple, k, for a given set of determinations. The formula was developed by Anderson and Bancroft[5] and is given by

$$k = \sum_i \sum_j f_{ij}\, n_{ij}^2$$

where

n_{ij} is the number of determinations at site i by lab j

$$f_{ij} = \frac{\left(\frac{1}{n_{ij}} - \frac{1}{n_i}\right)}{df}$$

n_i is the total number of determinations at site i

and

df is the degrees of freedom for labs.

As an example, we have the following sample sizes for the analysis of the Method 3 data:

$n_1 = 56$	$n_2 = 63$	$n_3 = 42$
$n_{11} = 14$	$n_{21} = 16$	$n_{31} = 12$
$n_{12} = 15$	$n_{22} = 16$	$n_{32} = 12$
$n_{13} = 14$	$n_{23} = 16$	$n_{33} = 7$
$n_{14} = 13$	$n_{24} = 15$	$n_{34} = 11$

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and there are 9 degrees of freedom. So

$$k = \sum_i \sum_j \frac{\left(\frac{1}{n_{ij}} - \frac{1}{n_i}\right)}{9} n_{ij}^2$$

$$= \frac{1}{9} \sum_i \sum_j \left(\frac{1}{n_{ij}} - \frac{1}{n_i}\right) n_{ij}^2$$

$$= \frac{1}{9} \left[\left(\frac{1}{14} - \frac{1}{56}\right)(14^2) + \ldots + \left(\frac{1}{11} - \frac{1}{42}\right)(11^2)\right]$$

$$= 13.37.$$

Thus, we can say that for the labs/sites factor, the expected mean square is $\sigma^2 + (13.37)\sigma_L^2$, and using this relationship we can estimate σ_L^2 from the AOV table.

C.2 Precision Estimates For % CO_2

This section presents the analysis of variance table and develops the variance estimates for the % CO_2 determination. There were 161 determinations used, which results in a total degrees of freedom of 160 for this analysis. Of this number, 2 are attributed to the site factor. The labs/sites degrees of freedom are obtained by taking the number of labs at a site less one and summing for all sites, or $3(4 - 1) = 9$. The remaining degrees of freedom are attributed to the error term, which is calculated from the repetitions within each laboratory at each site. The AOV is summarized in Table C-1.

TABLE C.1 ANALYSIS OF VARIANCE FOR % CO_2.

Source	DF	SS	MS	F	EMS
Sites	2	1222.82	611.41	*	*
Labs/Sites	9	152.84	16.98	8.24†	$\sigma^2 + (13.37)\sigma_L^2$
Error	149	306.59	2.06		σ^2
Total	160	1682.25			

*Not of interest.
†Significant value at 5% level.

The F value for labs/sites is the ratio of the mean square for labs/sites to the mean square for error. This ratio exceeds the critical value of 1.95, taken from a table of the F-distribution at the 5 percent level of significance with 9 and 149 degrees of freedom. This implies that there is a laboratory effect, or equivalently, that the laboratory bias variance, σ_L^2, is greater than zero.

Using the expected mean squares, we can obtain precision estimates for the within-laboratory and laboratory bias components. The expected mean square of the error term is σ^2, the within-laboratory variance. Thus, the estimated within-laboratory variance is the mean square for error, or

$$\hat{\sigma}^2 = 2.06.$$

This gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{2.06}$$

$$= 1.44\% \text{ } CO_2 \text{ by volume.}$$

This estimate has 149 degrees of freedom associated with it.

The laboratory bias variance is estimated from the labs/sites mean square. The manner of obtaining the expected mean square is discussed in Appendix C.1. Since the expected mean square is

$$EMS = \sigma^2 + 13.37\sigma_L^2,$$

σ_L^2 is estimated by

$$\delta_L^2 = \frac{MS_L - \delta^2}{13.37}$$

where MS_L is the mean square for labs/sites. Then

$$\delta^2 = \frac{16.98 - 2.06}{13.37}$$

$$= \frac{14.92}{13.37}$$

$$= 1.12.$$

The estimated laboratory bias variance has 9 degrees of freedom associated with it. The laboratory bias standard deviation, σ_L, is estimated as

$$\delta_L = \sqrt{\delta_L^2}$$

$$= \sqrt{1.12}$$

$$= 1.06\%\ CO_2 \text{ by volume.}$$

The between-laboratory variance, σ_b^2, is defined as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2.$$

Substituting the estimates for σ^2 and σ_L^2 gives

$$\delta_b^2 = \delta_L^2 + \delta^2$$

$$= (1.12) + (2.06)$$

$$= 3.18$$

and the between-laboratory standard deviation estimate is

$$\delta_b = \sqrt{3.18}$$

$$= 1.78\%\ CO_2 \text{ by volume.}$$

C.3 Precision Estimates For % O_2

The analysis of variance table for % O_2 determination is presented here, and the variance component estimates derived. There are 161 determinations used in the analysis, for a total of 160 degrees of freedom. Of these, $3 - 1 = 2$ are due to sites, while $3(4 - 1) = 9$ are due to labs/sites. The remainder form the error term. The analysis of variance table is shown in Table C.2.

TABLE C.2 ANALYSIS OF VARIANCE FOR % O_2.

Source	DF	SS	MS	F	EMS
Sites	2	2127.80	1063.90	-*	-*
Labs/Sites	9	225.37	25.04	8.63†	$\sigma^2 + (13.37)\sigma_L^2$
Error	149	432.55	2.90		σ^2
Total	160	2785.72			

*Not of interest.
†Significant value at 5% level.

The F-value shown for labs/sites is the ratio of the mean squares for labs/sites and error. The value exceeds the tabled value of 1.95 taken from a table of the F-distribution at the 5 percent significance level with 9 and 149 degrees of freedom. This implies that there is a significant laboratory effect on the O_2 determination, or that σ_L^2 is greater than zero.

Using the expected mean squares, the within-laboratory and laboratory bias variances may be estimated. The expected mean square for error is σ^2, the within-laboratory variance. Thus, the estimated within-laboratory variance is

$$\hat{\sigma}^2 = 2.90,$$

the mean square for error. There are 149 degrees of freedom associated with this variance estimate. The within-laboratory standard deviation, σ, is estimated as

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{2.90}$$

$$= 1.70\% \, O_2 \text{ by volume.}$$

The expected mean square for labs/sites is $\sigma^2 + (13.37)\sigma_L^2$. Then σ_L^2 is estimated by

$$\hat{\sigma}_L^2 = \frac{(MS_L - \hat{\sigma}^2)}{13.37}$$

where MS_L is the mean square for labs/sites. Thus,

$$\hat{\sigma}_L^2 = \frac{25.04 - 2.90}{13.37}$$

$$= \frac{22.14}{13.37}$$

$$= 1.66,$$

with 9 degrees of freedom. The estimated laboratory bias standard deviation, σ_L, is

$$\hat{\sigma}_L = \sqrt{1.66}$$

$$= 1.29\% \, O_2 \text{ by volume.}$$

The between-laboratory precision components are estimated from the above. The between-laboratory variance, σ_b^2, is estimated by

$$\hat{\sigma}_b^2 = \hat{\sigma}_L^2 + \hat{\sigma}^2$$

$$= (2.90) + (1.66)$$

$$= 4.56$$

The between-laboratory standard deviation, then, is estimated as

$$\hat{\sigma}_b = \sqrt{4.56}$$

$$= 2.14\ \%\ O_2 \text{ by volume.}$$

C.4 Precision Estimates For Dry Molecular Weight.

The dry molecular weight precision components are estimated by using an analysis of variance on the values in Table 3. There were 161 total determinations made, which gives 160 total degrees of freedom. The site factor accounts for $3 - 1 = 2$ of these, and the labs/sites accounts for $3(4 - 1) = 9$, the number of labs less one at each site, summed for the three sites. The remaining 149 degrees of freedom are attributable to the repetitions per lab, or error term. The analysis of variance table is shown in Table C.3.

TABLE C.3 ANALYSIS OF VARIANCE FOR DRY MOLECULAR WEIGHT

Source	DF	SS	MS	F	EMS
Sites	2	14.62	7.31	*	*
Labs/Sites	9	2.33	0.26	6.25†	$\sigma^2 + (13.37)\sigma_L^2$
Error	149	5.95	0.04		σ^2
Total	160	22.90			

*Not of interest.
†Significant at 5% level.

The F-value given for labs/sites is the ratio of the mean squares for labs/sites and error. This value may be said to be significant at the 5 percent level if it exceeds a tabled value taken from the F-distribution with 9 and 149 degrees of freedom. The critical value is 1.95, so that the labs/sites factor has a significant effect on the overall mean level. This is equivalent to saying that the laboratory bias variance, σ_L^2, is greater than zero.

To estimate the precision components, the expected mean square (*EMS*) column is used. The *EMS* of the error term is σ^2, the within-laboratory variance. Thus,

$$\hat{\sigma}^2 = MS_{\text{error}}$$

$$= 0.04$$

is the estimated within-laboratory variance, with 149 degrees of freedom. The within-laboratory standard deviation, then, is estimated by

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{0.04}$$

$$= 0.2 \text{ lb/lb-mole.}$$

The *EMS* of the labs/sites factor is $\sigma^2 + (13.37)\sigma_L^2$, as developed in Appendix C.1. Thus, the estimated laboratory bias variance is

$$\hat{\sigma}_L^2 = \frac{MS_L - \hat{\sigma}^2}{13.37}$$

where MS_L is the mean square for labs/sites. Then

$$\hat{\sigma}_L^2 = \frac{0.26 - 0.04}{13.37}$$

$$\delta_L^2 = \frac{0.22}{13.37}$$

$$= 0.02.$$

The laboratory bias variance estimate has 9 degrees of freedom associated with it. The estimated laboratory bias standard deviation is

$$\delta_L = \sqrt{0.02}$$

$$= 0.14 \text{ lb/lb-mole.}$$

The between-laboratory components are estimated using the above estimates. The between-laboratory variance is defined as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2,$$

so that the estimated value,

$$\delta_b^2 = \delta_L^2 + \delta^2$$

$$= (0.02) + (0.04)$$

$$= (0.06).$$

This gives an estimated between-laboratory variance of

$$\delta_b = \sqrt{0.06}$$

$$= 0.24 \text{ lb/lb-mole.}$$

C.5 Distribution of Excess Air.

The excess air determinations were used to propose a distribution model for these determinations which could predict the excess air percentage at a given level of O_2. The formula in the absence of CO, as derived in Section IV of the report,

$$\% EA = \frac{\% O_2}{(26.4) - (1.264)\% O_2 - (0.264)\% CO_2} \times 100 \text{ percent}$$

indicates that the chief contribution to the $\% EA$ was made by $\% O_2$. A model was proposed, then, that did not contain the $\% CO_2$ as an independent variable. Due to the nature of the determinations, an exponential model,

$$y = a_o e^{a_1 x}$$

was proposed where

y is $\% EA$

x is $\% O_2$

and

a_o, a_1, are unknown constants.

A least squares regression[6] is used to estimate a_o and a_1. Taking the natural log of the equation gives

$$\ln y = \ln a_o + a_1 x,$$

which is of the form

$$y' = a_o' + a_1 x.$$

This is the usual form of a simple linear regression, and by using the formulas

$$a_1 = \frac{\sum x_i y_i'/n - \bar{x}\bar{y}'}{\sum x_i^2/n - \bar{x}^2}$$

and

$$a_o' = \bar{y}' - a_1 \bar{x}$$

where

n is the total determinations used

$\bar{x}$ is the mean $\%\ O_2$

$\bar{y}'$ is the mean of the $(\ln y)$'s

the least squares estimates of a_o' and a_1 are obtained. These are derived using one quarter of the data points.

$$a_1 = 0.21$$

$$a_o' = 2.35$$

Then to fit the proposed model,

$$a_o' = \ln a_o$$

which implies

$$a_o = e^{a_o'}$$

$$= e^{(2.35)}$$

$$= 10.47.$$

Thus, we have

$$\%\ EA = (10.47)e^{(0.21)\%\ O_2}$$

The closeness of this model to the determinations is measured by the coefficient of determination, r^2. The formula for r^2 is

$$r^2 = \frac{\left[\sum_1^n (x_i - \bar{x})(y_i' - \bar{y}')\right]^2}{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y}')^2}$$

The value of r^2 was 0.993, which indicates an extremely good fit to the model.

C.6 Moisture Fraction Precision Estimates.

The moisture fractions which appear in Table 5 are used to develop precision estimates. The determinations are used in an analysis of variance on a nested design, with 150 total determinations used. This gives 149 total degrees of freedom. Of these, 2 are attributed to sites, while the labs/sites factor accounts for $(4-1)+(4-1)+(3-1)=8$ degrees of freedom, the number of labs per site less one, summed over all sites. The remaining 140 are attributed to the repetitions per lab or error term. The analysis of variance is summarized in Table C.4.

TABLE C.4 ANALYSIS OF VARIANCE FOR MOISTURE FRACTION

Source	DF	SS	MS	F	EMS
Sites	2	1.699	0.850	–*	–*
Labs/Sites	8	0.103	0.013	13.000†	$\sigma^2 + (13.78)\sigma_L^2$
Error	140	0.136	0.001		σ^2
Total	150	1.938			

*Not of interest.
†Significant at 5% level.

The F-value shown is the ratio of the labs/sites mean square to the error mean square. This value is significant at the 5 percent level if it exceeds the tabled value taken from the F-distribution with 8 and 140 degrees of freedom. The table value is approximately 2.02, which implies that there is a significant laboratory effect, or that the laboratory bias variance, σ_L^2, is greater than zero.

Using the expected mean squares, the variance components may be estimated. The EMS of the error term is σ^2, the within-laboratory variance. Thus the estimated value of σ^2 is

$$\hat{\sigma}^2 = 0.001$$

the error mean square. This estimate has 140 degrees of freedom associated with it. Then the estimated within-laboratory standard deviation is

$$\hat{\sigma} = \sqrt{0.001}$$

$$= 0.032.$$

The EMS of the labs/sites factor is $\sigma^2 + 13.78\sigma_L^2$. The factor 13.78 is obtained according to the formula in Appendix C.1, substituting the values for the sample sizes and degrees of freedom for this study. Thus

$$E(MS_L) = \sigma^2 + 13.78\sigma_L^2$$

where MS_L is the mean square for labs/sites. This implies

$$\hat{\sigma}_L^2 = \frac{MS_L - \hat{\sigma}^2}{13.78}$$

$$= \frac{0.013 - 0.001}{13.78}$$

$$= \frac{0.012}{13.78}$$

$$= 0.001$$

with 8 degrees of freedom. The estimated laboratory bias standard deviation, then, is

$$\hat{\delta}_L = \sqrt{0.001}$$

$$= 0.032.$$

The between-laboratory variance is $\sigma_b^2 = \sigma_L^2 + \sigma^2$. Substituting into this equation, gives

$$\hat{\sigma}_b^2 = \hat{\delta}_L^2 + \hat{\sigma}^2$$

$$= (0.001) + (0.001)$$

$$= (0.002).$$

From this, the estimated between-laboratory standard deviation is

$$\hat{\sigma}_b = \sqrt{0.002}$$

$$= 0.045.$$

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